Electronic polarity of nanoclusters: Quantum and many-body effects

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Interesting electrical polarity in nanoclusters usually requires the polarizability to exceed the value R^3 of the classical sphere of radius R. We clarify how this occurs naturally in single electron quantum systems, and relate it to the giant polarizability of $Na_{14}F_{13}$, and to spontaneous dipole formation on niobium clusters. Many-body effects generally reduce the polarizability through screening. The usual random phase approximation (RPA) treatment retrieves the classical answer, but it significantly overestimates screening in few-electron systems. The system of two electrons on the surface of a sphere is solved numerically, to account for the Coulomb repulsion. At high densities, numerical results agree with the RPA model with properly subtracted self-interaction effects. At low densities, the system performs quantum oscillations around the classical ground state. We calculate the lowest anharmonic correction to the polarizability, which also agrees well with numerical evaluation of the polarizability.

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I. INTRODUCTION

Electrical polarity[1,2] (both permanent moments μ_0 and induced moments $\mu_{\text{ind}}=\alpha F_{\text{ext}}$) are important in determining the interaction of a nanocluster with its environment[3] and with external probes such as light.[4] Large polarizability may also lead to spontaneous symmetry-breaking, analogous to bulk ferroelectricity.[5–7] Despite good numerical progress on the polarizability[8] of small systems, its general understanding is not developed. In classical electrostatics, a metallic sphere of radius R placed in an external electric field $\vec{F}$ develops surface charge whose field exactly cancels the external field in the interior. The dipole $\vec{\mu}=\alpha\vec{F}$ associated with this surface charge gives the polarizability of a classical metal sphere, $\alpha_{\text{CMS}}=R^3$. Experiments on various metallic clusters[9] and on C_{60}[10] yield values of α in rough agreement.[11] However, larger α is necessary for spontaneous dipole formation. For example, in a crystal of nearly touching point-polarizable spheres, the Clausius-Mossotti polarization catastrophe occurs when $4\pi n\alpha/3>1$, where n is the concentration. This translates to a critical polarizability of $\alpha_c=3\sqrt{2}R^3/\pi$, larger than the available metallic value.

How could larger-than-classical values of α emerge in metallic clusters? An analog case is the prediction[5] and apparent confirmation[12] that the system $Na_{n+1}Cl_n$ (and especially the highly symmetric $Na_{14}Cl_{13}$ case), with one electron in a loosely-bound "surface state" outside a closed shell, has a second-order Jahn-Teller instability to a polar state. This suggests that the total polarizability (α_{el}=electronic plus $\Sigma Z_{\text{eff}}^2/\omega^2$=vibrational, with Z_{eff} being appropriate Born effective charges and ω the relevant vibrational frequencies[13]) has diverged. Similarly, de Heer's group[6] found low T permanent dipole moments on Nb clusters which might be interpreted as $\alpha(T)$ increasing to a divergence as T decreases.

In this paper, we analyze the polarizability of a nanocluster with a surface state occupied by an electron. As a model for this system, we consider an electron confined to the surface of a sphere. We show that due to quantum effects, electronic polarizability can considerably exceed the metallic value α_{CMS} at low temperatures. This result implies that the coupling between the surface electron and elastic modes of nuclear displacement can decrease the vibrational frequencies and drive the total polarizability to diverge. We also analyze how the classical value α_{CMS} is recovered by screening when the number of metallic electrons increases. In particular, we consider the case of two surface electrons which is realized in the neutral cluster $Mg_{14}O_{13}$. We predict that when a second electron is added, the polarizability diminishes to values closer to α_{CMS}, and stability of the symmetric structure is restored.

II. POLARIZABILITY OF ONE ELECTRON ON THE SPHERE

Confining electrons to the surface of a sphere permits theoretical simplification.[15] This model is not as much of a "spherical cow"[16] as might be thought. For example, the C_{60} molecule confines 60 carbon π electrons to the region near the surface of a sphere. In neutral undistorted $Na_{14}Cl_{13}$, one outer electron lies in a shell similar to a sphere. "Core-shell" nanoparticles with insulating cores and metallic shells have been studied.[17] The electron eigenstates are $\psi_L=Y_L(\Omega)$, the spherical harmonics, with $L=(\ell,m)$, and energies $E_L=(\hbar^2/2mR^2)\ell(\ell+1)$. The polarizability $\alpha=\langle\mu_z\rangle/F_z$ is

$$\alpha(T)=2\sum_{LL'} w_L\frac{|\langle L'|\mu_z|L\rangle|^2}{E_L-E_L'}, \tag{1}$$

where the dipole operator μ_z is $-eR\cos\theta$ and $w_L=w_\ell=\exp(-E_L/k_BT)/Z$ is the probability that the system is in state L. At $T=0$, the electron is in the ground state ($w_L=\delta_{L,0}$), and there is only one nonzero matrix element, $\langle 1,0|\cos\theta|0,0\rangle=1/\sqrt{3}$. Then we get

$$\alpha(T=0)=\frac{2R^4}{3a_B}, \tag{2}$$

where a_B is the Bohr radius. This result is interesting, because it shows that for unscreened one-electron systems, the value of α can exceed the value $\alpha_{CMS}=R^3$. The scaling with R^4/a_B is not restricted to the spherical shell, but is general for finite system with one electron, e.g., a cubic box. The high temperature ($k_BT \gg \hbar^2/mR^2$) answer can be found from classical statistical mechanics, and is given by Debye-Langevin law (Ref. 24):

$$\alpha(\text{high } T)=\frac{e^2R^2}{3k_BT}. \tag{3}$$

The crossover from the $T=0$ quantum result to the classical limit occurs at the temperature $k_BT_* \approx \hbar^2/2mR^2$. Consider the outer electron of $Na_{14}F_{13}$, responsible for the giant polarizability measured by Rayane *et al.*[19] The T dependence can be interpreted as a large low T value from Eq. (2), which evolves at higher T toward the classical value of Eq. (3). At intermediate temperatures, the polarizability can be easily tabulated numerically. Using the well-known matrix elements of a dipole moment (Ref. 18)

$$\langle l+1,m|\cos\theta|l,m\rangle = i\sqrt{\frac{(\ell+1-m)(\ell+1+m)}{(2\ell+1)(2\ell+3)}}, \tag{4}$$

one can rewrite Eq. (1)

$$\alpha(T)=6\alpha(0)\sum_{\ell}\left(\frac{w_\ell - w_{\ell+1}}{(\ell+1)(\ell+2)-\ell(\ell+1)}\right) \times \sum_{m=-\ell}^{\ell}\frac{(\ell+1)^2-m^2}{(2\ell+1)(2\ell+3)}. \tag{5}$$

The sum over m can now be done, giving

$$\alpha(T)=\alpha(0)\sum_{\ell}(w_\ell - w_{\ell+1})=\alpha(0)w_0=\alpha(0)/Z. \tag{6}$$

The computation reduces to calculation of the partition function $Z=\Sigma_\ell(2\ell+1)e^{-\ell(\ell+1)/\tau}$, with the dimensionless temperature $\tau=T/T_*$. Figure 1 shows values of $\alpha(T)$ from Eq. (6) plotted versus $1/\tau$ and compared with the data[19] for $Na_{14}F_{13}$. Two fitting parameters were used: the value $\alpha(0)$ was taken to be 1950 Å (Ref. 3) and the crossover temperature $T_*=\hbar^2/2mR^2=975$ K. Using Eq. (2), one finds reasonable values, $R=4.1$ Å and an effective mass $m^*=5.3$ free electron masses. (Of course, rotational and vibrational sources of T dependence of α are probably not negligible, but the limited experimental range of T does not warrant a closer fit.) For comparison, based on the Na-F bond length $a=2.3$ Å, one can estimate the cluster size to be about $R=4$ Å. Note that the low temperature polarizability is much larger than $\alpha_{CMS}=70$ Å^3.

One can consider an alternative explanation of the $1/T$ behavior of the susceptibility. One can imagine that the cluster in fact has a large spontaneous dipole moment with fixed orientation with respect to cluster. Thermal rotations in the absence of an external electric field would randomize the direction of polarization, and an external field would align the dipole. Any mechanism of this sort, however, would produce saturation temperature much smaller than T_* because of a large mass associated with dipole rotations. This would be clearly incompatible with the saturation temperature observed in Ref. 19.

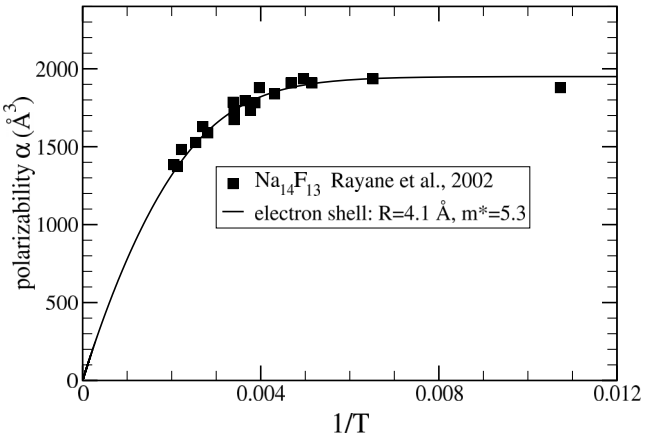

FIG. 1. Polarizability versus inverse temperature in K for $Na_{14}F_{13}$ clusters from Ref. 19, compared with theory for a single electron on a sphere.

In our calculation, we assumed that the response is linear in the applied field. For this assumption to be valid, the polarization energy $\alpha\mathcal{E}^2/2$ must be smaller than the level spacing $\hbar^2/mR^2$. For larger fields, the dipole moment would saturate. One can estimate the saturation field as $\mathcal{E}_{\text{sat}}=\mathcal{E}_{\text{at}}(a_B/R)^3$, where $\mathcal{E}_{\text{at}}=e/a_B^2$ is atomic electric field, which is of the order of 10^{10} V/m. One can see from this estimate that although the saturation field quickly decays with the cluster radius, it is still rather large for reasonable values of R.

III. SCREENING EFFECTS

If there are many electrons on the shell, a mean field [random phase approximation (RPA) or time-dependent Hartree] approximation may be reasonable. In Refs. 15 and 20, polarizability was derived via RPA. Below we give a simple derivation and discuss the effects due to a finite number of electrons. Consider the metallic sphere containing N electrons in the external field $\mathcal{E}$. The electric potential on the surface of the sphere is generated both by the external electric field source and electrons. In polar coordinates, the external field contribution is $-\mathcal{E}r\cos\theta$, while the dipole moment contribution is $\mu_z\cos\theta/r^2$ for $r \geqslant R$. In the mean field theory, electrons respond to the screened potential on the surface $r=R$, which is proportional to the effective field $\mathcal{E}_{\text{eff}}=\mathcal{E}-\mu_z/R^3$. The self-consistency condition is then

$$\mu_z=\alpha_0\mathcal{E}_{\text{eff}}=\alpha_0\left(\mathcal{E}-\frac{\mu_z}{R^3}\right). \tag{7}$$

Solving Eq. (7) for μ_z, one arrives at

$$\alpha_{\mathrm{MF}} = \frac{\alpha_0}{1 + \alpha_0/R^3}. \tag{8}$$

This calculation overestimates screening effects: the actual field acting on an electron should not include the field created by the electron itself. Assuming that all electrons contribute equally to the screening field, one can exclude self-interaction by multiplying the screening field $-\mu_z/R^3$ by $(1-1/N)$. The result

$$\alpha_{\mathrm{MFC}} = \frac{\alpha_0}{1 + (1-1/N)\alpha_0/R^3}, \tag{9}$$

unlike Eq. (8), behaves correctly at $N=1$.

A realization of a dense metallic spherical shell is the π-electron system of the C_{60} molecule.[20] Pederson and Quong[21] computed the polarizability of C_{60} both without and with self-consistent screening. Their answer for α_0 is 35 a_B^3 per C atom, while after screening they find α_{MF} to be 9.3 a_B^3 per C atom. The electrons are on a spherical shell which is more than infinitesimally thin, but let us use the thin model anyway. To account for the reduction by screening, we need $R=9.0a_B$. This compares reasonably with the radius 6.7 -7.0 a_B of the carbon nuclei, adding an extra Angstrom of distance for the finite extent of the π electron system.

IV. TWO-ELECTRON MODEL

The Coulomb interaction between electrons leads to correlation between their positions, which is omitted in mean field theory. To clarify the role of correlation, we consider two electrons on the sphere. Related studies of few-electron model systems exist[22,23] but polarizability was not analyzed. We use the Hamiltonian

$$H = -\frac{\hbar^2}{2mR^2}(\boldsymbol{\nabla}_1^2 + \boldsymbol{\nabla}_2^2) + \frac{e^2}{R|\mathbf{n}_1 - \mathbf{n}_2|}, \tag{10}$$

where $\mathbf{n}_{1,2}$ are positions of the electrons on the sphere ($\mathbf{n}_{1,2}^2=1$), and $\boldsymbol{\nabla}_{1,2}^2$ are spherical Laplace operators. The first term in Eq. (10) represents the kinetic energy, and the second term describes Coulomb repulsion between electrons. The polarizability at $T=0$ is again given by Eq. (1), with $|L\rangle$ being exact two-particle states, E_L their energies, and $\mu_z=eR(n_{z1}+n_{z2})$ being the total dipole moment. There are multiple states with a given total angular momentum L'. The sum in Eq. (1) is taken over all such states.

Solving for eigenstates of the Hamiltonian (10) is difficult even at zero temperature because of a vast configuration space. To reduce its dimension, we use symmetry considerations. The ground state $\Psi_0(\mathbf{n}_1,\mathbf{n}_2)$ is symmetric with respect to electron coordinates and has total angular momentum $\ell=0$. Thus, the mass center of the two-electron system is completely delocalized, and Ψ_0 only depends on the distance between the electrons. We use the spherical angle γ to parametrize this distance ($\cos\gamma=\mathbf{n}_1\cdot\mathbf{n}_2$), so the wave function takes the form $\Psi_0(\mathbf{n}_1,\mathbf{n}_2)=\Psi_0(\gamma)$. To compute the action of the kinetic energy term $\boldsymbol{\nabla}_{1,2}^2$ in Eq. (10) on $\Psi_0(\mathbf{n}_1,\mathbf{n}_2)$, it is convenient to use the following trick. Note that the kinetic energy in the $\ell=0$ state also depends on the relative angle γ only, and therefore one can compute it at some particular values of $\mathbf{n}_{1,2}$ and extend the result for all $\mathbf{n}_{1,2}$ with the same value of γ. A convenient point corresponds to the second electron at the north pole. Then, the angle γ equals the polar angle of the first electron, and the kinetic energy is given by the well-known expression for the Laplace operator on the sphere. Treating the second electron in the same manner, one obtains the Schrödinger equation for $\ell=0$ states:

$$\left\{-\frac{\hbar^2}{mR^2}\frac{1}{\sin\gamma}\frac{\partial}{\partial\gamma}\left(\sin\gamma\frac{\partial}{\partial\gamma}\right) + U_{\ell=0}(\gamma)\right\}\Psi_0(\gamma) = E_0\Psi_0(\gamma), \tag{11}$$

where the effective potential

$$U_{\ell=0}(\gamma) = \frac{e^2}{2R\sin\frac{\gamma}{2}} \tag{12}$$

is entirely due to the Coulomb interaction.

Now consider excited states. The only nonzero matrix elements in Eq. (1) are between $\ell=0$ and $\ell=1$ states. Moreover, since both Ψ_0 and μ_z are symmetric with respect to permutation of the electrons, one has to consider only those $\ell=1$ states in which electron momenta are added symmetrically. Up to a scalar multiplier, one can construct only one symmetric vector out of $\mathbf{n}_{1,2}$: $\mathbf{N}=(\mathbf{n}_1+\mathbf{n}_2)/\left(2\cos\frac{\gamma}{2}\right)$ (we normalized $\mathbf{N}$ so that $\mathbf{N}^2=1$). In other words, the transformation properties of $\ell=1$ states are identical to those of the mass center of the system. The wave function of the states with $\ell=1$, $\ell_z=0$ therefore can be written in the form $\Psi_1^{(n)}\times(\mathbf{n}_1,\mathbf{n}_2)=N_z\Psi_1^{(n)}(\gamma)$. By a direct calculation, we find that the Schrödinger equation for $\Psi_1(\gamma)$ has a form similar to Eq. (11) with a different effective potential:

$$U_{\ell=1}(\gamma) = U_{\ell=0}(\gamma) + \frac{\hbar^2}{4mR^2}\left(1 + \frac{1}{\cos^2\frac{\gamma}{2}}\right). \tag{13}$$

The last contribution in Eq. (13) is the kinetic energy of joint rotation of the two electrons with angular momentum $L=1$. One can derive this "centripetal" term by a different method. At fixed distance between the electrons γ, the rotational dynamics of the two-electron system can be described as that of a quantum asymmetric top with moments of inertia $I_1=2mR^2\sin^2\gamma/2$, $I_2=2mR^2$, and $I_3=2mR^2\sin^2\gamma/2$. It is known (see, e.g, Ref. 25) that $\ell=1$ is a special case in the quantum top problem: the wave functions of these states are completely determined by the symmetry and therefore independent of $I_{1,2,3}$. In our case it means that the top dynamics is independent of oscillations of γ. This allows one to separate the variables for $\ell=1$ state. The wave function of the two electron system can be written as $\Psi_1(\mathbf{n}_1,\mathbf{n}_2)=\Psi_T(\xi,\eta,\zeta)\Psi_\gamma(\gamma)$, where Ψ_T is the wave function of the top described by Euler angles ξ, η, and ζ. (One can also check that this top wave function is proportional to $\mathbf{N}$.) For symmetric $\ell=1$ states with zero projection of J on the top axis, the energy of the top is $\frac{\hbar^2}{2}(1/I_1+1/I_2)$, which coincides with the last term in Eq. (13).

One can now use Eqs. (11)–(13) to find eigenfunctions and eigenvalues by solving a one-dimensional boundary-value problem. [The wave function has to be regular everywhere on the sphere. However, a general solution to Eq. (11) may have singularities at $\gamma=0$ and $\gamma=\pi$, where the coefficients of Schrödinger equation are singular. Thus, the requirement of regularity at these points serves as two independent boundary conditions.] While in the limit of $R \ll a_B$ one can thus reproduce the mean field theory result (9), the opposite limit of strong interaction ($R \gg a_B$) is more interesting. In this regime, Coulomb repulsion dominates over kinetic energy. In the ground state, electrons perform zero-point oscillations at opposite poles of the sphere, thus minimizing potential energy. The electric field shifts the minimum and changes the energy of the system. The extra energy due to the field is $U_{\mathcal{E}}(\gamma)=2e\mathcal{E}_{\perp}R\cos\gamma/2$, where $\mathcal{E}_{\perp}$ is the field component perpendicular to the axis connecting electrons. Minimizing the potential energy $U_{\ell=0}(\gamma)+U_{\mathcal{E}}(\gamma)$, one finds the ground state energy to be $e^2/2R-4R^3\mathcal{E}_{\perp}^2$. Averaging over all directions of the axis, one can replace $\mathcal{E}_{\perp}^2$ by $2\mathcal{E}^2/3$. Thus, the polarizability of the two-electron system in the classical limit is $16R^3/3$, still higher than the metallic value.

However, it turns out that the amplitude of zero point motion around the equilibrium positions decays only as $(a_B/R)^{1/4}$, and the simple classical picture described above holds only for impractically large values $R/a_B > 10^4$. To improve the classical approximation, one can expand Eqs. (11)–(13) in the vicinity of the classical equilibrium, $\gamma \approx \pi$. For the $\ell=0$ state, Schrödinger equation takes the form:

$$\frac{\hbar^2}{mR^2}(\hat{h}_0+\delta\hat{h}_0)\Psi_0(x)=E_0\Psi_0(x), \tag{14}$$

where $x=\pi-\gamma$ is the deviation from equilibrium. The dimensionless Hamiltonian

$$\hat{h}_0=-\frac{\partial^2}{\partial x^2}-\frac{1}{x}\frac{\partial}{\partial x}+\frac{R}{2a_B}\left(1+\frac{x^2}{2}\right) \tag{15}$$

describes harmonic oscillations near the equilibrium, and

$$\delta\hat{h}_0=\frac{x}{3}\frac{\partial}{\partial x}+\frac{5}{3\cdot 128}\frac{R}{a_B}x^4 \tag{16}$$

is the first anharmonic correction to $\hat{h}_0$. For $\ell=1$, one finds a similar equation with harmonic and anharmonic parts given by

$$\hat{h}_1=\hat{h}_0+\frac{1}{x^2};\quad \delta\hat{h}_1=\delta\hat{h}_0+\frac{1}{3}. \tag{17}$$

If one ignores anharmonic parts, these equations can be satisfied by wave functions of a harmonic oscillator:

$$\psi_0(x)=\exp(-x^2/2x_0^2), \tag{18}$$

$$\psi_1(x)=x\psi_0(x), \tag{19}$$

where

$$x_0=(4a_B/R)^{1/4} \tag{20}$$

is the amplitude of zero point oscillations. The corresponding eigenvalues are

$$E_0=\frac{e^2}{2R}\left(1+\sqrt{\frac{a_B}{R}}\right);\quad E_1=\frac{e^2}{2R}\left(1+2\sqrt{\frac{a_B}{R}}\right). \tag{21}$$

The first term $e^2/2R$ is the classical Coulomb energy, and the second term is due to quantum oscillations.

The zero point motion amplitude x_0 can be considered as a small anharmonicity parameter. We shall now compute anharmonic corrections to the polarizability, expanding over the powers of x_0^2. Treating anharmonic terms δh_0 and δh_1 by standard perturbation theory, one can compute the corrections to the energy levels:

$$\delta E_0=\langle\psi_0|\delta\hat{h}_0|\psi_0\rangle=-\frac{e^2}{R}\frac{x_0^4}{16},$$

$$\delta E_1=\langle\psi_1|\delta\hat{h}_1|\psi_1\rangle=\frac{e^2}{R}\frac{5x_0^4}{16}. \tag{22}$$

Similarly, one can also find corrections to the wave functions

$$\delta\psi_0=\frac{x_0^2}{2}\left(-\frac{\xi^4}{24}-\frac{\xi^2}{9}-\frac{1}{36}\right)e^{-\xi^2/2},$$

$$\delta\psi_1=\frac{x_0^2}{2}\left(\frac{5\xi^5}{144}-\frac{\xi^3}{16}-\frac{\xi}{12}\right)e^{-\xi^2/2}, \tag{23}$$

where $\xi=x/x_0$.

One can now use $\delta E_{0,1}$ and $\delta\psi_{0,1}$ to calculate the correction to the polarizability given by Eq. (1). To do that, one has to take into account anharmonic corrections to the dipole moment operator:

$$\mu=2eR\mathbf{N}\cos\frac{\gamma}{2}\approx 2eR\mathbf{N}x_0\xi\left(1-\frac{\xi^2x_0^2}{24}\right) \tag{24}$$

(here $\mathbf{N}$ is the unit vector directed to the mass center), and to the volume element in the integral:

$$d\Omega\propto\sin\gamma d\gamma\approx x_0^2\left(1-\frac{\xi^2x_0^2}{6}\right)\xi d\xi. \tag{25}$$

(One can check that this volume element is consistent with kinetic part of the Hamiltonian.) In the lowest order in anharmonic corrections, the only important contribution comes from the lowest $\ell=1$ state. The contributions of higher $\ell=1$ states are absent in harmonic approximation, and their contributions to the matrix element are proportional to anharmonicity parameter x_0^2. Since the polarization contains square of the matrix element, excited $J=1$ states contribute only in the fourth order in x_0, which we do not consider here. Substituting Eq. (24) into Eq. (1) and replacing the matrix element of N_z between $J=0$ and $J=1$ states by $1/\sqrt{3}$, one finds:

$$\alpha=\frac{2e^2R^2}{3}\frac{x_0^2}{E_1+\delta E_1-E_0-\delta E_0}\frac{M^2}{N_0N_1}, \tag{26}$$

where

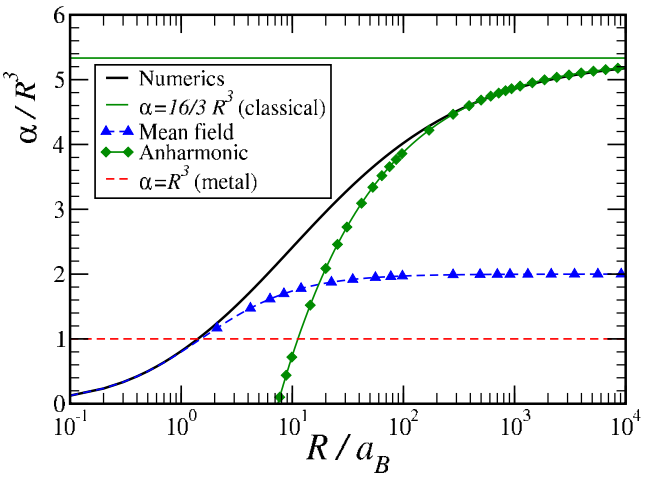

FIG. 2. (Color online) Polarizability of two electrons on a sphere vs its radius R, normalized to the classical value R^3 on a logarithmic scale. The mean field [Eq. (9) and anharmonic Eq. (31)] results are also shown for comparison.

$$M = 2\int_0^\infty \xi^2 d\xi \left(1 - \frac{5\xi^2 x_0^2}{24}\right)(\psi_0 + \delta\psi_0)(\psi_1 + \delta\psi_1) \quad (27)$$

and $N_{0,1}$ are normalization integrals, with corrected volume element:

$$N_i = 2\int_0^\infty \left(1 - \frac{\xi^2 x_0^2}{6}\right)(\psi_i + \delta\psi_i)^2 \xi d\xi. \quad (28)$$

Substituting wave function corrections (23), one finds, in the lowest order:

$$N_0 = 1 - \frac{7x_0^2}{18}; \quad N_1 = 1 - \frac{x_0^2}{3};$$

$$M = 1 - \frac{2x_0^2}{3}. \quad (29)$$

The energy difference, according to Eqs. (21) and (22), is

$$E_1 - E_0 + \delta E_1 - \delta E_0 = \frac{e^2}{R}\left(\frac{x_0^2}{4} + \frac{3x_0^4}{8}\right). \quad (30)$$

Substituting Eqs. (29) and (30) into Eq. (26), one finally obtains:

$$\alpha_2(R \gg a_B) \approx \frac{16R^3}{3}\left(1 - \frac{49}{36}x_0^2\right) = \frac{16R^3}{3}\left[1 - \frac{49}{18}\left(\frac{a_B}{R}\right)^{1/2}\right]. \quad (31)$$

The results of numerical solution of the two-electron problem are shown on Fig. 2. The self-consistent result (9) breaks down at $R \sim 3a_B$, while the classical regime (31) takes over at $R \geq 100a_B$. For reasonable size nanoclusters ($R \sim 10a_B$), the effect of electron correlations is significant, but the polarizability is still considerably higher than the classical value $\alpha = R^3$.

The limit $R < a_B$ shown in the left part of the plot may seem unphysical. However, note that the Bohr radius entering our calculation is in fact an effective parameter, depending on the effective mass of the surface state. If, for some reasons, the effective state is a light electron, the effective Bohr radius can also be large, and the limit $R < a_B$ may become physically applicable.

It is also instructive to check whether the Clausius-Mossotti catastrophe ($4\pi/3n\alpha > 1$) can be achieved. Packing spheres in the most dense way, one requires $\alpha/R^3 > 3\sqrt{2}/\pi$, which is achieved for $R \geq 2.5a_B$. Thus, despite screening, an array of two-electron nanoclusters can develop a spontaneous polarization.

To summarize, the polarizability of a nanocluster with a surface electron state may be significantly enhanced due to quantum effects. This enhancement, however, disappears when the number of "metallic" electrons is increased. Although we considered a very simple model of a nanocluster, our results should hold qualitatively for more complex clusters, including niobium ferroelectric clusters studied in Ref. 6. At the first sight, these clusters do not look like single-electron systems. However, if the spectrum of the high T state has its outermost electron in a separated level with orbital degeneracy, as in Na_3 (see Ref. 14), or with quasi-Jahn-Teller degeneracy as in $Na_{14}Cl_{13}$, similar physics probably applies. Also, despite the fact that we only considered surface electrons, one can expect a similar physics when electrons are confined in the bulk of the cluster. The estimate for the level spacing, dipole moment and therefore for polarizability, should be still valid for bulk electrons. As an example of bulk confinement, one may consider electrons confined by a parabolic potential $U(r) = m\Omega^2 r^2/2$. If the electron is in the ground state which has size R of order of zero point motion amplitude $R \sim \sqrt{\hbar/m\Omega}$, the dipole matrix element is also of the order of R, and energy spacing between the ground state and the first excited state is of the order of $\hbar^2/mR^2 = \hbar\Omega$. Therefore, one finds the polarizability to be of the order of R^4/a_B. Thus, our results can give correct qualitative description for more complex clusters with a small number of "mobile" electrons.

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